

Supporting Information

A Sulfur(VI) Fluoride Exchange Click Chemistry Approach towards Main Chain Liquid Crystal Polymers Bearing Sulfate Ester Groups

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GENERAL CONSIDERATIONS.

Materials and Instruments

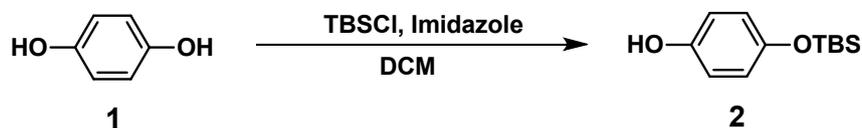
Dicyclohexylcarbodiimide (DCC), dimethylaminopyridine (DMAP), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), triazabicyclodecene (TBD) and 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diaza-phosphorine (BEMP) were purchased from Aladdin (Shanghai) Inc. 1,2,4-Trichlorobenzene (TCB) and *tert*-butyldimethylsilyl chloride (TBS-Cl) were obtained from Macklin Inc. Sulfuryl fluoride gas (SO₂F₂) was obtained from Shangfluoro Inc.

A Sigma 2K 15 centrifuge was used for isolation of polymers after precipitation. All flash chromatography were performed using Macherey-Nagel MN Kieselgel 60 (0.063-1.2 mm). All ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were obtained using a Bruker HD 600MHz spectrometer or a Bruker HW300 MHz spectrometer at 295 K and recorded in CDCl₃ or 1,2-dichlorobenzene-d₄. Gel permeation chromatography (GPC) was performed on an PL-GPC220 high pressure liquid chromatography (HPLC), equipped with an HP 1047A refractive index detector and a Plgel MIXED-C 300-7.5 mm column (packed with 5 μm particles). The column packing allowed the separation of polymers over a wide molecular weight range of 200-3000000. TCB was used as the eluent at a flow rate of 1 mL/min at 150 °C. Polystyrene standards were used as the references. Differential scanning calorimetry (DSC) spectra were recorded on a TA Instruments Q20 instrument (New Castle, DE) under nitrogen purge at a heating rate of 10 K/min from 0 °C to +250 °C. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA7.

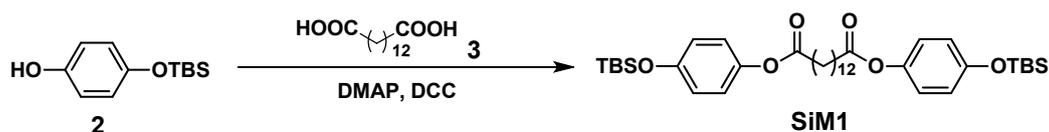
Polarized optical microscopy (POM) observations of the liquid crystalline (LC) textures of all the monomers and polymers were performed on an Olympus BX53P microscope with a Mettler PF82HT hot stage. The images were captured by using a Microvision MV-DC200 digital camera with a Phenix Phmias 2008 Cs Ver2.2 software. X-ray scattering experiments were performed with a high-flux small angle X-ray scattering instrument (SAXSess, Anton Paar) equipped with a Kratky block-collimation system and a temperature control unit (Anton Paar TCS300). At each single steady temperature, both small angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) were simultaneously recorded on an imaging-plate (IP) which was extended to high-angle range (the q range covered by the IP was from 0.06

nm^{-1} to 29 nm^{-1} , $q = 4\pi(\sin\theta)/\lambda$, where the wavelength λ is 0.1542 nm of $\text{Cu K}\alpha$ radiation and 2θ is the scattering angle) at 40 kV and 40 mA for 30 min .

Synthesis of monomer SiM1

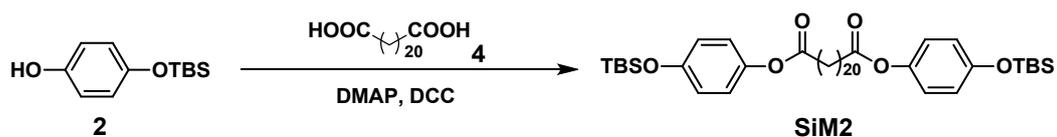


Step 1: A mixture of hydroquinone (13.2 g , 120 mmol), imidazole (5.4 g , 80 mmol) and dichloromethane (200 mL) were added into a 500 mL three-neck round-bottom flask. A solution of TBS-Cl (6.0 g in 30 mL dichloromethane) was slowly added into the above mixture. After stirring for 12 h , the solvent was removed by rotary evaporation and the crude compound was purified by flash chromatography (hexane: EtOAc = 2: 1) to give the desired intermediate **2** as a colorless oil (5.6 g , yield: 62%). $^1\text{H NMR}$ (600 MHz , CDCl_3) δ 6.72 (s, 4H), 4.52 (s, 1H), 1.00 (s, 9H), 0.18 (s, 6H).



Step 2: A mixture of DMAP (0.391 g , 3.2 mmol), compound **2** (3.589 g , 16 mmol), compound **3** (2.067 g , 8 mmol) and dichloromethane (100 mL) were added into a 250 mL three-neck round-bottom flask and stirred at $0 \text{ }^\circ\text{C}$. After slowly adding DCC (3.962 g , 19.2 mmol), the reaction solution was stirred at $0 \text{ }^\circ\text{C}$ for 15 min and then continuously stirred at room temperature for another 48 h . The solvent was removed by rotary evaporation and the crude compound was purified by flash chromatography (hexane: EtOAc=10 :1) to give the desired monomer **SiM1** as a white solid (4.342 g , yield: 81%). $^1\text{H NMR}$ (600 MHz , CDCl_3) δ 6.76 (dd, $J = 16.8$, 8.4 Hz , 4H), 6.64 (dd, $J = 16.7$, 8.4 Hz , 4H), 2.35 (dt, $J = 16.4$, 7.1 Hz , 4H), 1.64 - 1.50 (m, 4H), 1.25 - 1.07 (m, 16H), 0.95 - 0.75 (m, 18H), 0.17 - 0.05 (m, 12H). $^{13}\text{C NMR}$ (151 MHz , CDCl_3) δ 172.6 , 153.1 , 144.7 , 122.2 , 120.4 , 77.2 , 77.0 , 76.8 , 34.3 , 29.5 , 29.2 , 29.1 , 25.6 , 24.9 , 18.1 , 4.4 .

Synthesis of monomer SiM2

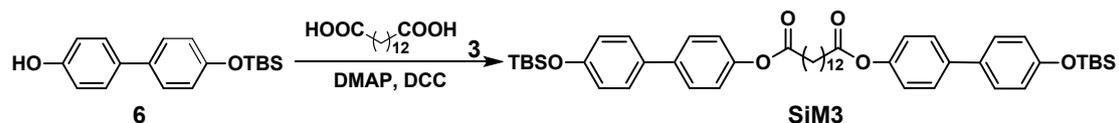


DMAP (0.147 g, 1.2 mmol), compound **2** (1.346 g, 6 mmol), compound **4** (1.112 g, 3 mmol) were dissolved in 100 mL of dichloromethane and stirred at 0 °C. After slowly adding DCC (1.483 g, 7.2 mmol), the above mixture was stirred at 0 °C for 15 min and then continuously stirred at room temperature for another 48 h. After evaporation of the solvent, the residual solid was purified by column chromatography on silica gel using hexane/EtOAc (30/1) as eluent to give desired monomer **SiM2** as a white solid (2.042 g, yield: 87%). ¹H NMR (600 MHz, CDCl₃) δ 6.74 (d, *J* = 8.6 Hz, 4H), 6.62 (d, *J* = 8.6 Hz, 4H), 2.33 (t, *J* = 7.2 Hz, 4H), 1.58-1.51 (m, 4H), 1.18-1.05 (m, 32H), 0.79 (s, 18H), -0.00 (s, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 172.4, 155.3, 149.6, 138.5, 133.4, 128.0, 127.6, 121.7, 120.3, 77.2, 77.0, 76.8, 34.4, 29.5, 29.1, 25.6, 24.9, 18.2, -4.3.

Synthesis of monomer SiM3



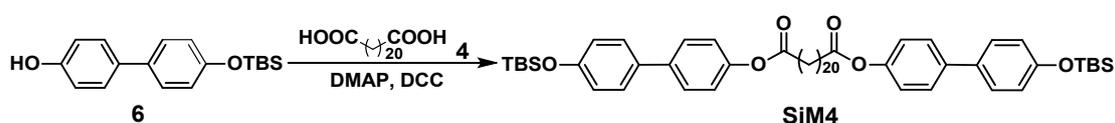
Step 1: A mixture of 4,4'-biphenol (16.8 g, 90 mmol), imidazole (4.0 g, 60 mmol) and dichloromethane (200 mL) were added into a 500 mL three-neck round-bottom flask. A solution of TBDMSCl (4.5 g in 30 mL dichloromethane) was slowly added into the above mixture and continuously stirred for 12 h. The solvent was removed by rotary evaporation and the crude compound was purified by flash chromatography (hexane: EtOAc= 2 :1) to give compound **6** as a white solid (5.1 g, yield: 57%). ¹H NMR (600 MHz, CDCl₃) δ 7.44 (dd, *J* = 15.2, 8.5 Hz, 4H), 6.91 (t, *J* = 7.6 Hz, 4H), 4.88 (d, *J* = 62.1 Hz, 1H), 1.04 (d, *J* = 2.8 Hz, 9H), 0.26 (d, *J* = 3.4 Hz, 6H).



Step 2: DMAP (0.196 g, 1.6 mmol), compound **6** (2.402 g, 8 mmol), compound **3** (1.034 g, 4 mmol) were dissolved in 100 mL of dichloromethane and stirred at 0 °C. After slowly adding DCC (1.980 g, 9.6 mmol), the reaction solution was stirred at 0 °C for 15 min and continuously stirred at room temperature for another 48 h. The

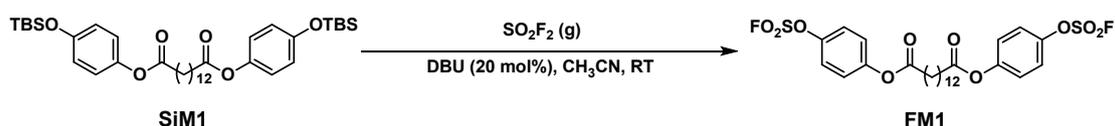
solvent was removed by rotary evaporation and the crude compound was purified by flash chromatography (hexane: EtOAc= 20:1) to give the desired monomer **SiM3** as a white solid (2.568 g, yield: 78%). ¹H NMR (600 MHz, CDCl₃) δ 7.55 (d, *J* = 8.7 Hz, 4H), 7.45 (d, *J* = 8.6 Hz, 4H), 7.14 (d, *J* = 8.7 Hz, 4H), 6.92 (d, *J* = 8.6 Hz, 4H), 2.59 (t, *J* = 7.5 Hz, 4H), 1.79 (dt, *J* = 15.2, 7.6 Hz, 4H), 1.34 (d, *J* = 18.5 Hz, 16H), 1.02 (s, 18H), 0.25 (s, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 172.4, 155.3, 149.6, 138.5, 133.4, 128.0, 127.6, 121.7, 120.3, 77.2, 77.0, 76.8, 34.4, 29.5, 29.2, 29.1, 25.6, 24.9, 18.2, -4.3.

Synthesis of monomer **SiM4**



A mixture of DMAP (0.147 g, 1.2 mmol), compound **6** (1.802 g, 6 mmol), compound **4** (1.112 g, 3 mmol) and dichloromethane (100 mL) were added into a 250 mL three-neck round-bottom flask and stirred at 0 °C. After slowly adding DCC (1.483 g, 7.2 mmol) the above mixture was stirred at 0 °C for 15 min and continuously stirred at room temperature for another 48 h. After evaporation of the solvent, the residual solid was purified by column chromatography on silica gel using hexane/EtOAc (50/1) as eluent to give the desired compound **SiM4** as a white solid (2.048 g, yield: 73%). ¹H NMR (600 MHz, CDCl₃) δ 6.74 (d, *J* = 8.9 Hz, 4H), 6.62 (d, *J* = 8.9 Hz, 4H), 2.33 (t, *J* = 7.5 Hz, 4H), 1.58 – 1.51 (m, 4H), 1.18 – 1.05 (m, 32H), 0.79 (s, 18H), -0.00 (s, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 172.4, 155.3, 149.6, 138.5, 133.4, 128., 127.6, 121.7, 120.3, 77.2, 77.0, 76.8, 34.4, 29.5, 29.2, 29.1, 25.6, 24.9, 18.2, -4.3.

Synthesis of monomer **FM1**



A mixture of **SiM1** (670 mg, 1 mmol) and dry acetonitrile (10 mL) were added into a 25 mL Schlenk-type flask and stirred. The flask was degassed and exchanged with SO₂F₂. DBU (30.4 mg, 0.2 mmol) was injected into the flask by syringe. After stirring at room temperature for 12 h, the reaction mixture was quenched with 1 M

HCl (10 mL) and extracted twice with EtOAc (10 mL \times 2). The organic extracts were washed with brine (20 mL), dried over anhydrous Na₂SO₄, filtered and concentrated. The product **FM1** was obtained as a white solid (565 mg, 93% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.35 (t, J = 6.2 Hz, 4H), 7.22 – 7.18 (m, 4H), 2.57 (t, J = 7.5 Hz, 4H), 1.78 – 1.71 (m, 4H), 1.43 – 1.37 (m, 4H), 1.37 – 1.28 (m, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 171.81 (s), 150.36 (s), 147.01 (s), 123.57 (s), 122.03 (s), 77.25 (s), 77.04 (s), 76.83 (s), 34.28 (s), 29.49 (d, J = 17.7 Hz), 29.24 (s), 29.07 (s), 24.81 (s). ¹⁹F NMR (282 MHz, CDCl₃) δ 38.44 (s).

Synthesis of P1

SiM1 (67.0 mg, 1 mmol) and **FM1** (60.6 mg, 1 mmol) were added in a 10 mL Schlenk flask. The flask was degassed and exchanged with N₂ *via* three cycles. A 0.1 mL of DBU solution (30.4 mg in 1 mL TCB) was added into above mixture and continuously stirred at 80 °C for 12 h. The reaction mixtures were then heated to dissolve any precipitated polymer (in some cases additional TCB was necessary to achieve complete dissolution) and the resulting homogenous solution was directly poured into ~100 mL of methanol to precipitate polymers. The collected solid was further dissolved in TCB and re-precipitated from methanol. After three cycles, the product was dried in high vacuum for 24 h to give the desired polymer **P1** as a white solid (57.3 mg, yield: 57%). ¹H NMR (300 MHz, 1,2-dichlorobenzene-d₄) δ 7.16 (d, J = 6.7 Hz, 4H), 7.09 (s, 4H), 2.54 (t, J = 7.0 Hz, 4H), 1.74 (s, 4H), 1.30 (d, J = 13.0 Hz, 16H).

Synthesis of P2

SiM2 (78.2 mg, 0.1 mmol) and **FM1** (60.6 mg, 0.1 mmol) were added in a 10 mL Schlenk flask. The flask was degassed and exchanged with N₂. A 0.1 mL solution of DBU (30.4 mg/mL) in TCB was added into above mixture and continuously stirred at 80 °C for 12 h. The reaction mixtures were then heated to dissolve any precipitated polymer (in some cases additional TCB was necessary to achieve complete dissolution) and the resulting homogenous solution was directly poured into ~100 mL of methanol to precipitate polymers. The collected solid was further dissolved in TCB and re-precipitated from methanol. After three cycles, the product was dried in high vacuum for 24 h to give the desired polymer **P2** as a white solid (68.5 mg, yield:

61%). ^1H NMR (300 MHz, 1,2-dichlorobenzene- d_4) δ 7.21 – 7.11 (m, 4H), 7.09 (s, 4H), 3.01-2.66 (m, 4H), 2.05 (s, 4H), 1.60 (d, $J = 30.7$ Hz, 16H).

Synthesis of P3

SiM3 (82.3 mg, 1 mmol) and **FM1** (60.6 mg, 1 mmol) were added in a 10 mL Schlenk flask. The flask was degassed and exchanged with N_2 *via* three freeze-thaw cycles. A 0.1 mL solution of DBU (30.4 mg/mL) in TCB was added into above mixture and continuously stirred at 80 °C for 12 h. The reaction mixtures were then heated to dissolve any precipitated polymer (in some cases additional TCB was necessary to achieve complete dissolution) and the resulting homogenous solution was directly poured into ~100 mL of methanol to precipitate polymers. The collected solid was further dissolved in TCB and re-precipitated from methanol. After three cycles, the product was dried in high vacuum for 24 h to give the desired polymer **P3** as a white solid (55.8 mg, yield: 48%). ^1H NMR (300 MHz, 1,2-dichlorobenzene- d_4) δ 7.72 (d, $J = 7.7$ Hz, 4H), 7.43 (s, 4H), 7.35 (s, 4H), 2.54 (t, $J = 7.3$ Hz, 4H), 1.83-1.69 (m, 4H), 1.36 (d, $J = 36.4$ Hz, 32H).

Synthesis of P4

SiM4 (93.5 mg, 1 mmol) and **FM1** (60.6 mg, 1 mmol) were added in a 10 mL in a Schlenk-type flask. The flask was degassed and exchanged with N_2 *via* three freeze-thaw cycles. A 0.1 mL solution of DBU (30.4 mg/mL) in TCB was added into above mixture and continuously stirred at 80 °C for 12 h. The reaction mixtures were then heated to dissolve any precipitated polymer (in some cases additional TCB was necessary to achieve complete dissolution) and the resulting homogenous solution was directly poured into ~100 mL of methanol to precipitate polymers. The collected solid was further dissolved in TCB and re-precipitated from methanol. After three cycles, the product was dried in high vacuum for 24 h to give the desired polymer **P4** as a white solid (57.1 mg, yield: 45%). ^1H NMR (300 MHz, 1,2-dichlorobenzene- d_4) δ 7.70 (d, $J = 8.2$ Hz, 4H), 7.41 (s, 4H), 7.35 (s, 4H), 2.73 – 2.41 (m, 4H), 1.78 (s, 4H), 1.19 (m, 32H).

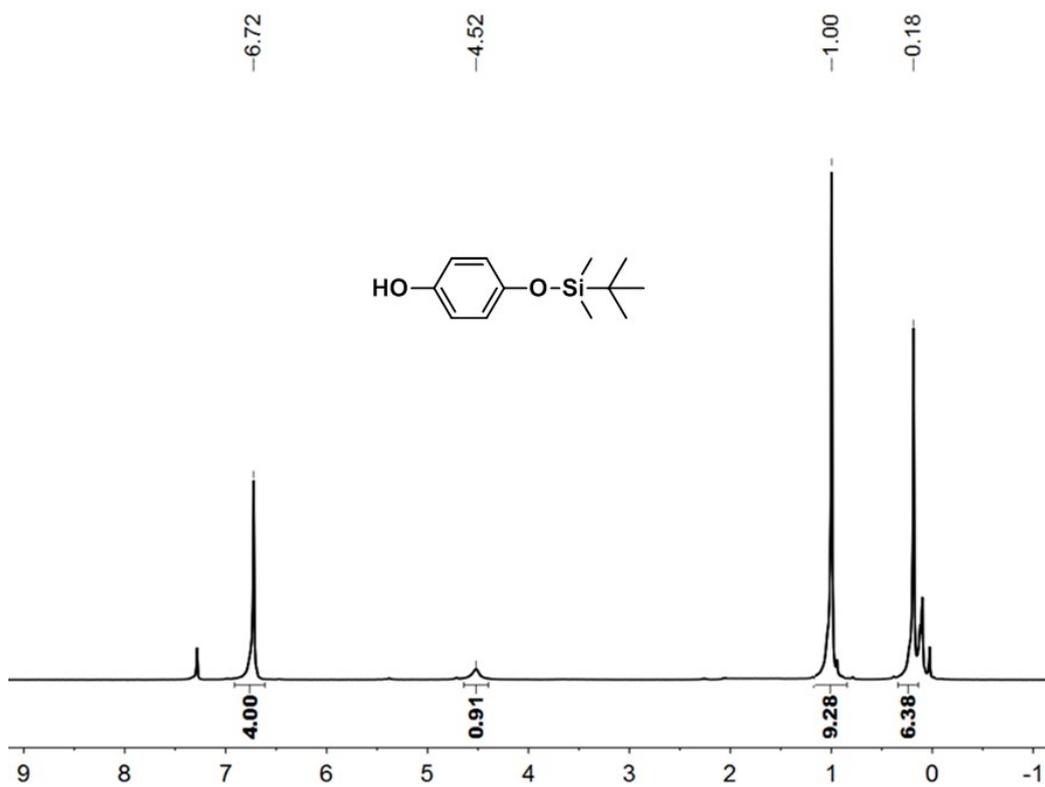


Figure S1. ¹H NMR spectrum of Compound 2.

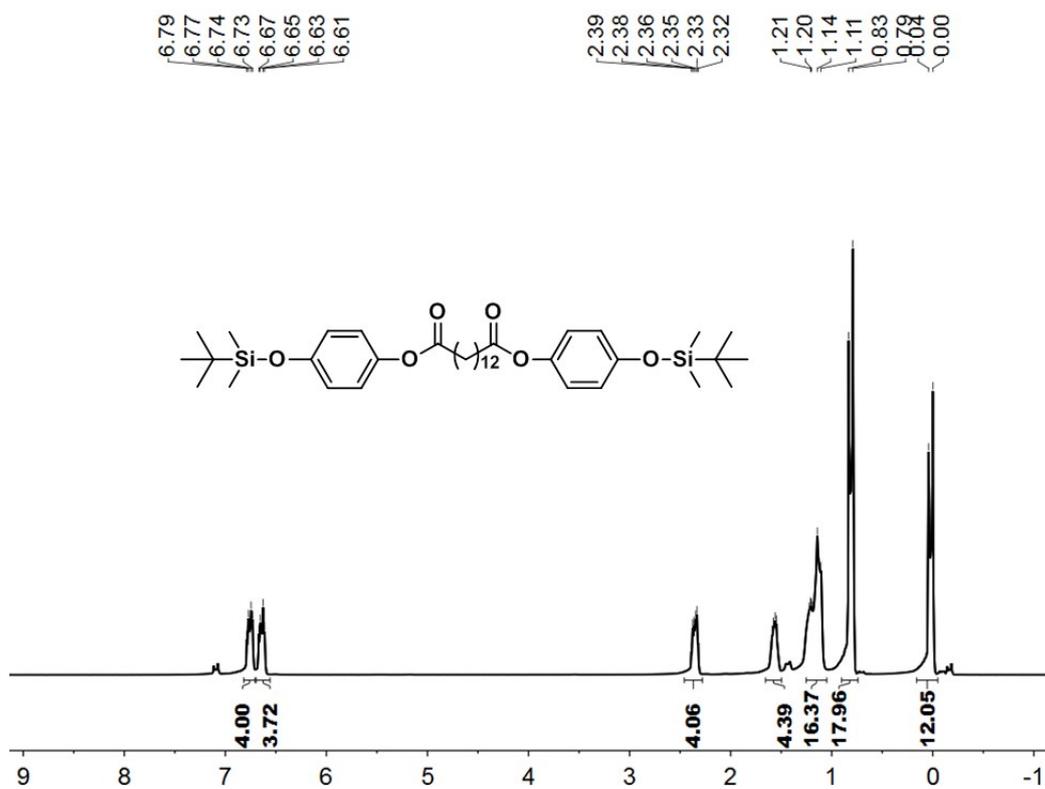


Figure S2. ¹H NMR spectrum of SiM1.

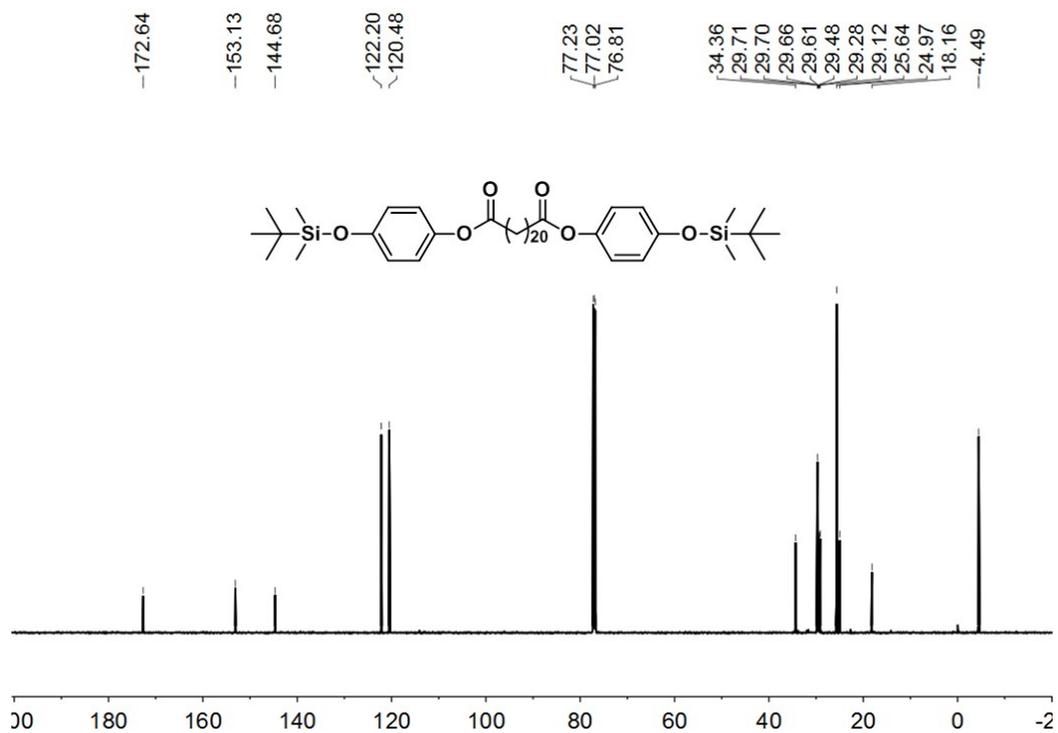


Figure S5. ¹³C NMR spectrum of SiM2.

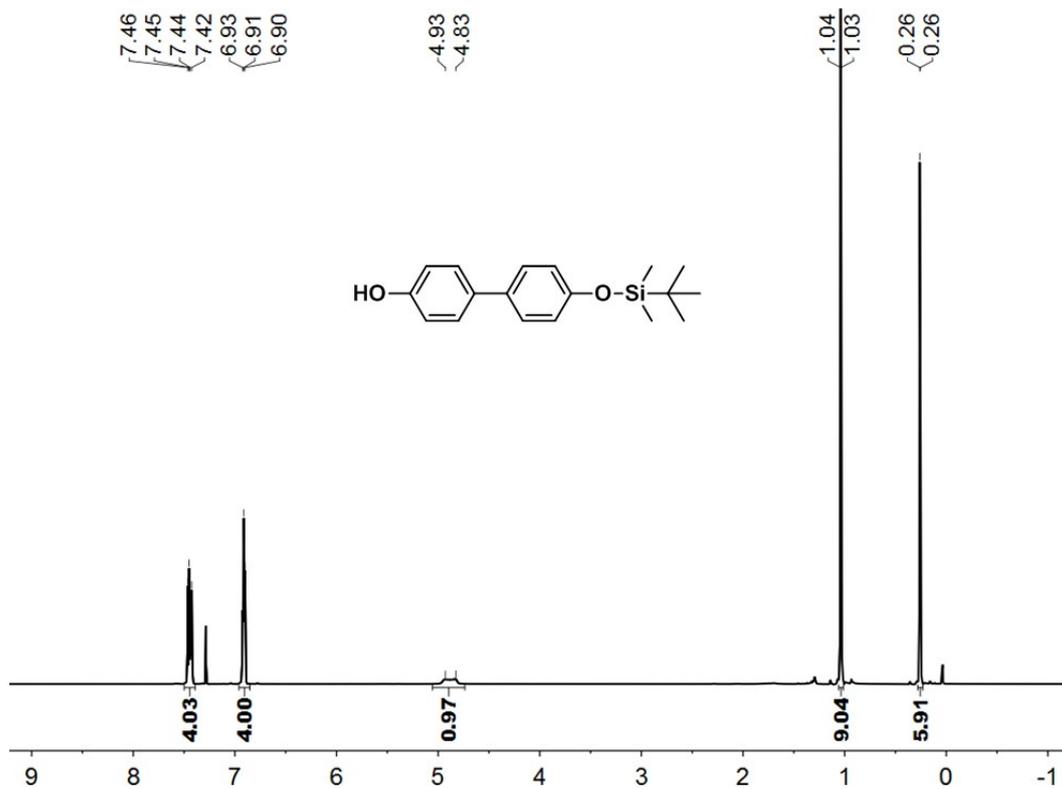


Figure S6. ¹H NMR spectrum of Compound 6.

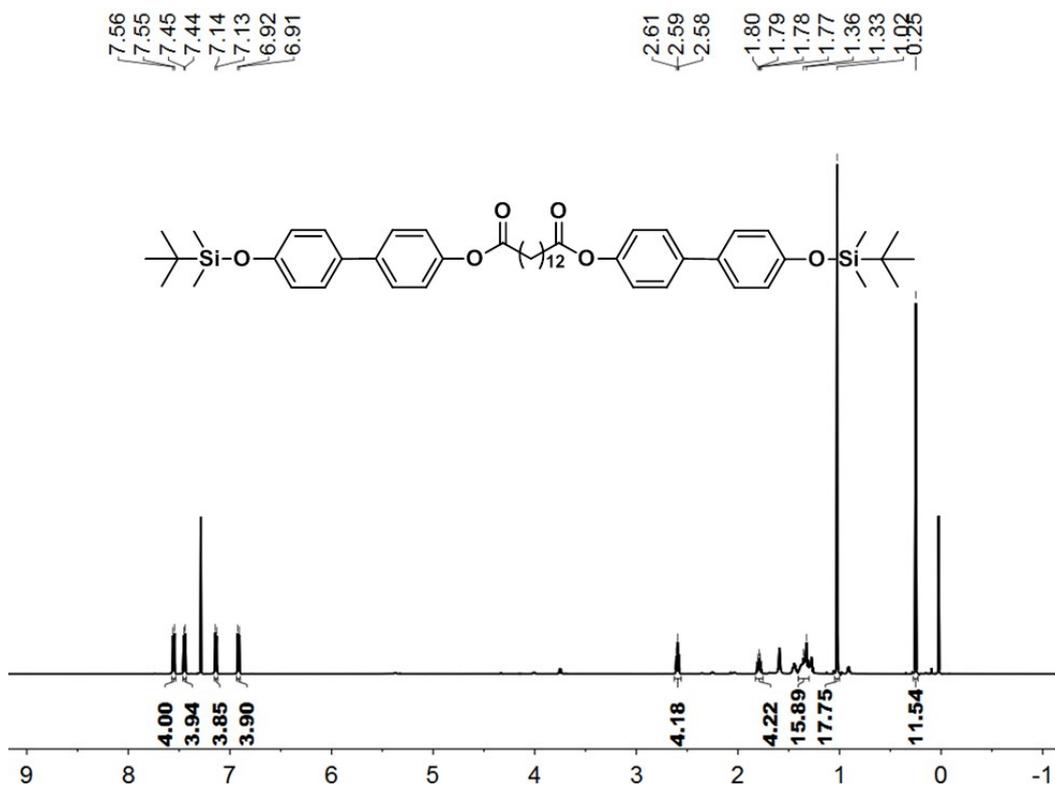


Figure S7. ¹H NMR spectrum of SiM3.

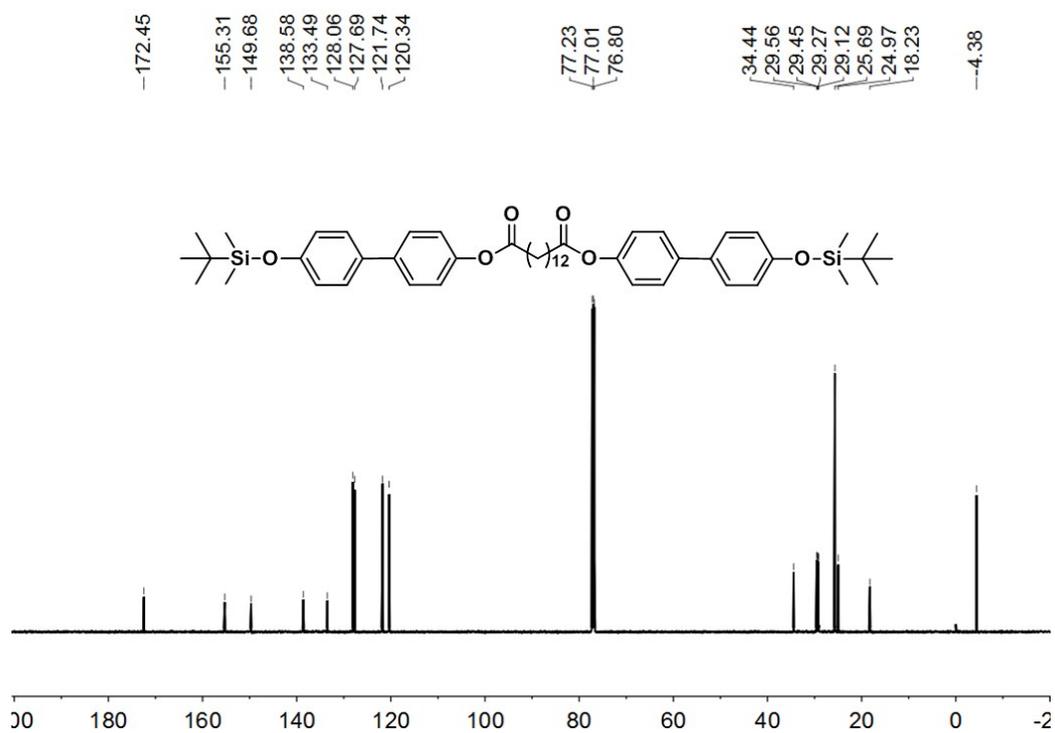


Figure S8. ¹³C NMR spectrum of SiM3.

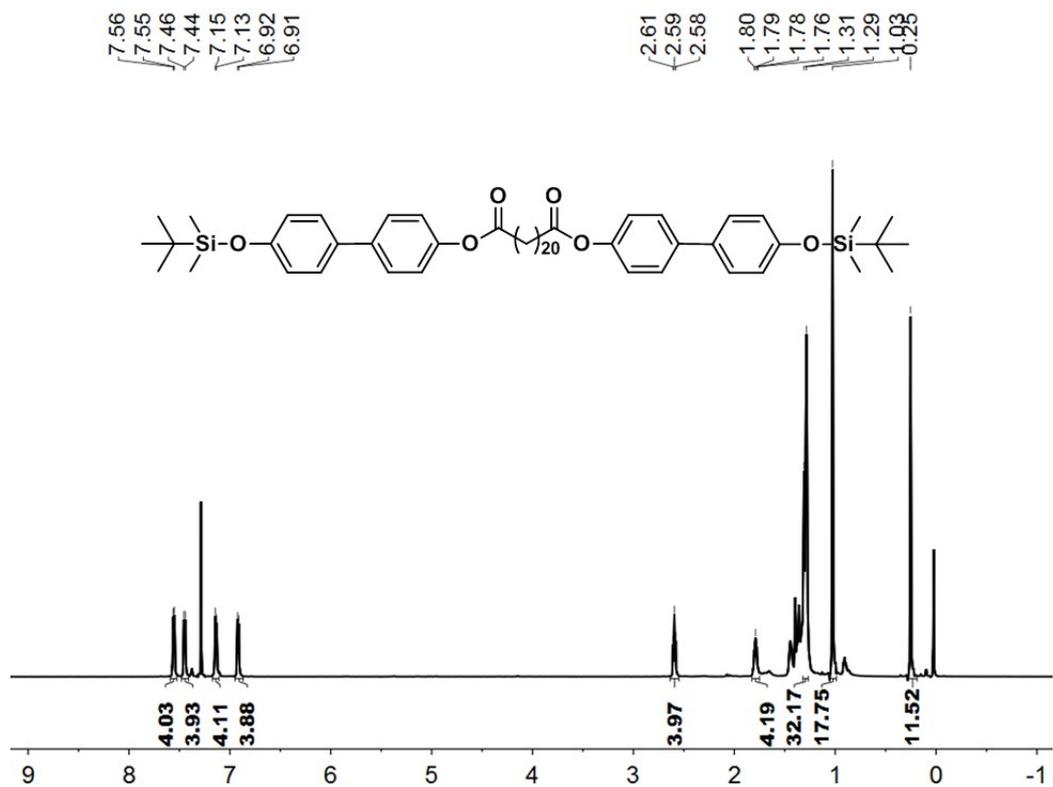


Figure S9. ¹H NMR spectrum of SiM4.

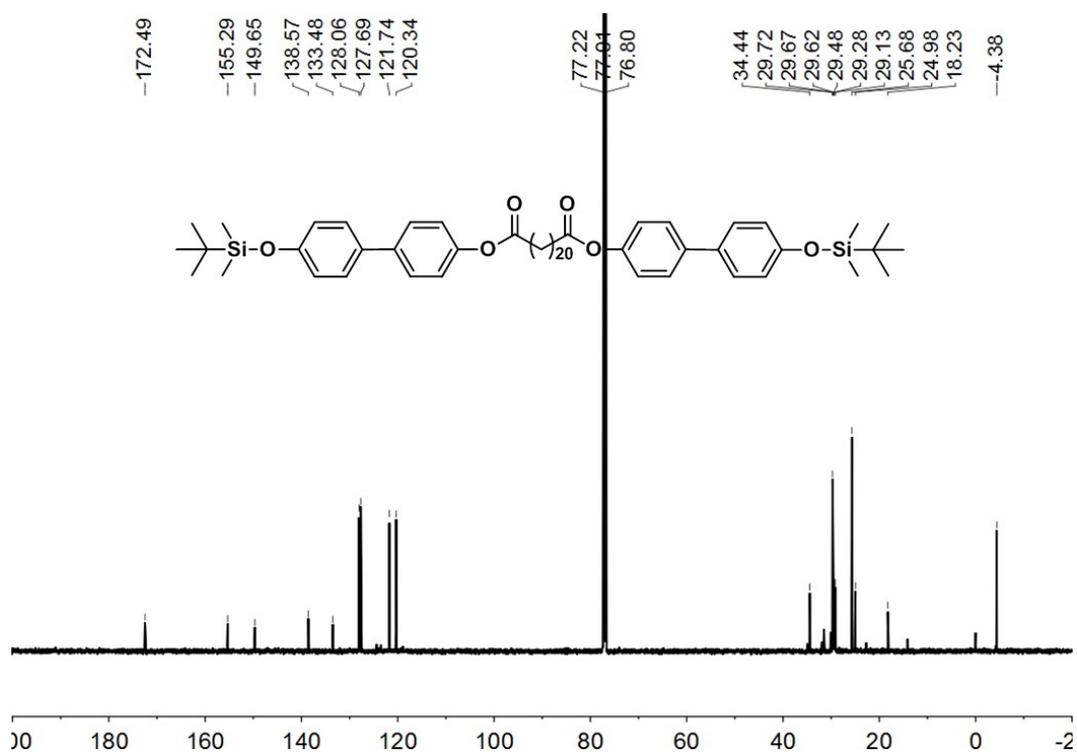


Figure S10. ¹³C NMR spectrum of SiM4.

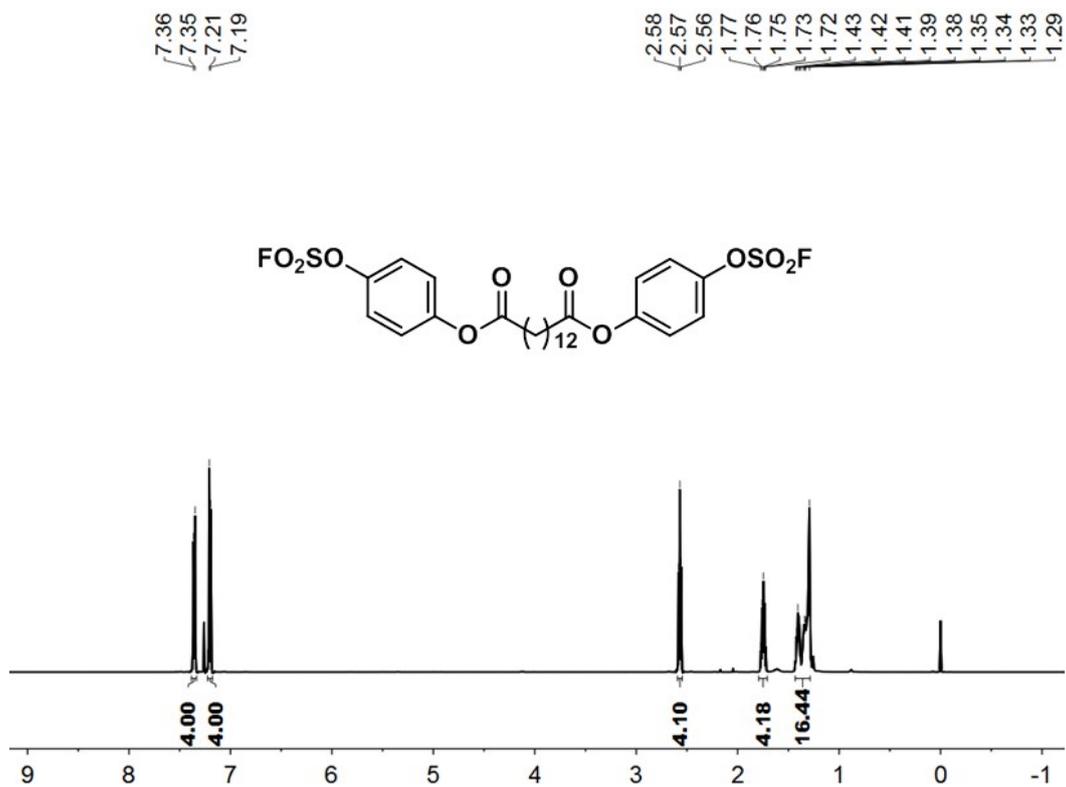


Figure S11. ¹H NMR spectrum of FM1.

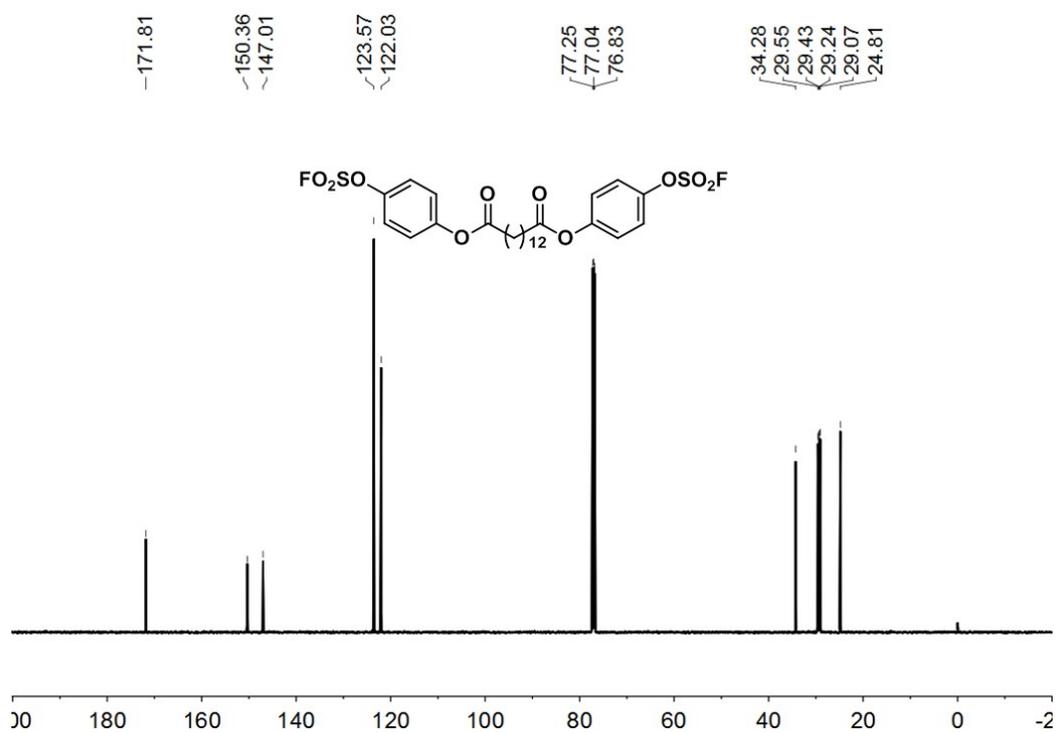


Figure S12. ¹³C NMR spectrum of FM1.

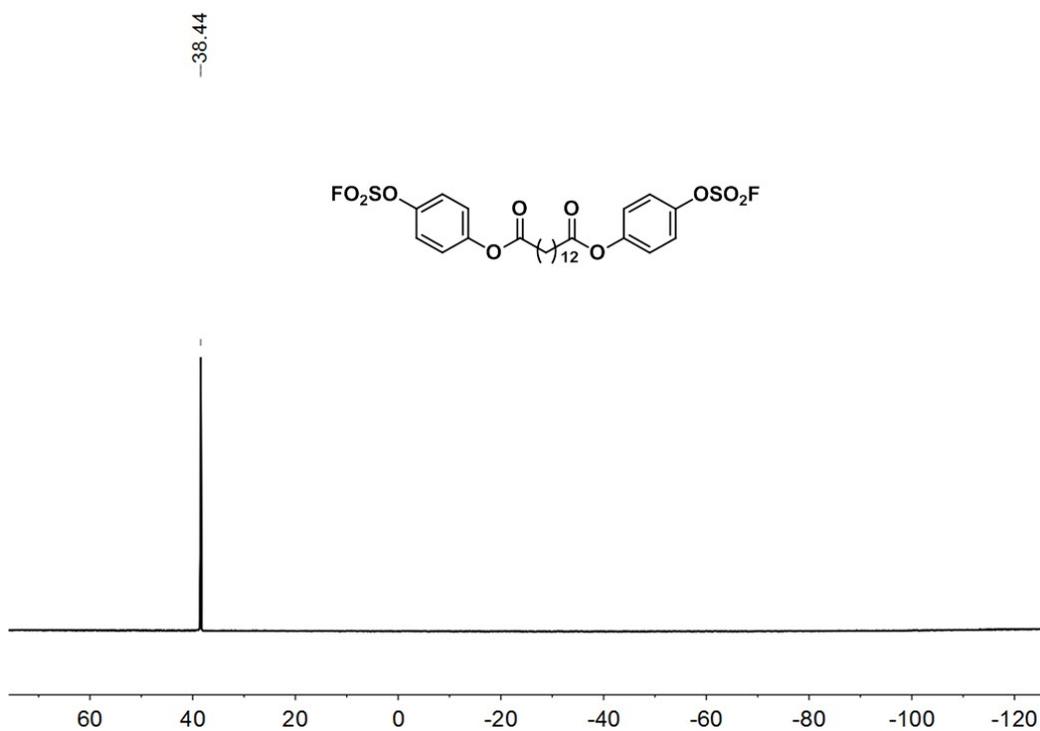


Figure S13. ^{19}F NMR spectrum of FM1.

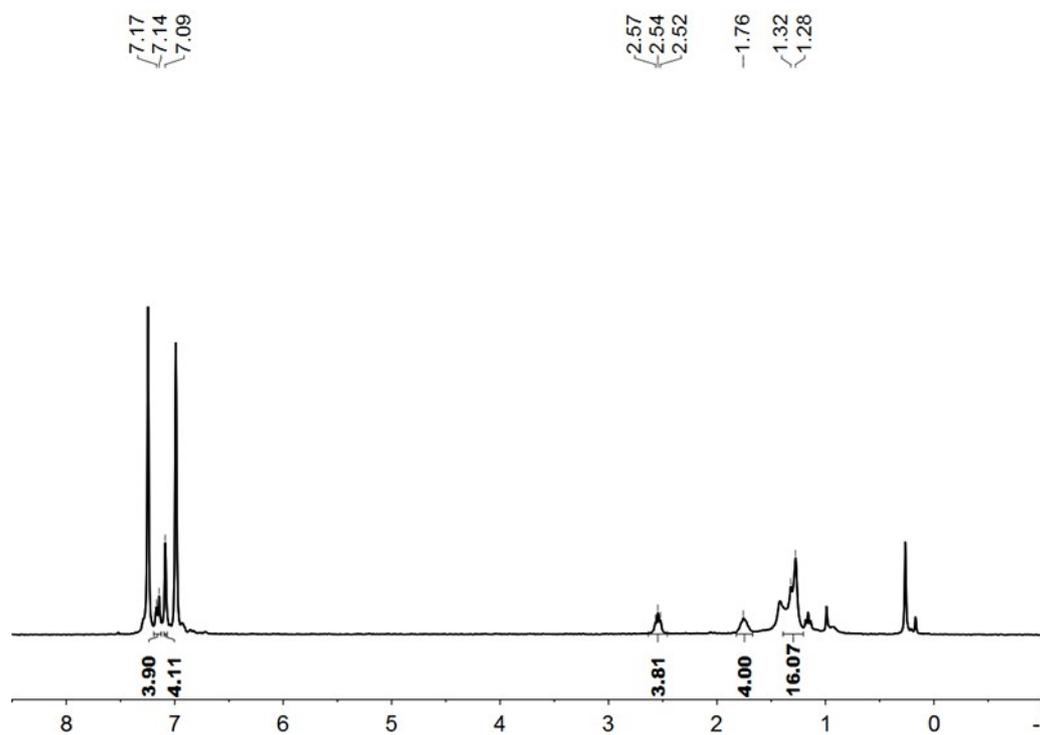


Figure S14. ^1H NMR spectrum of P1.

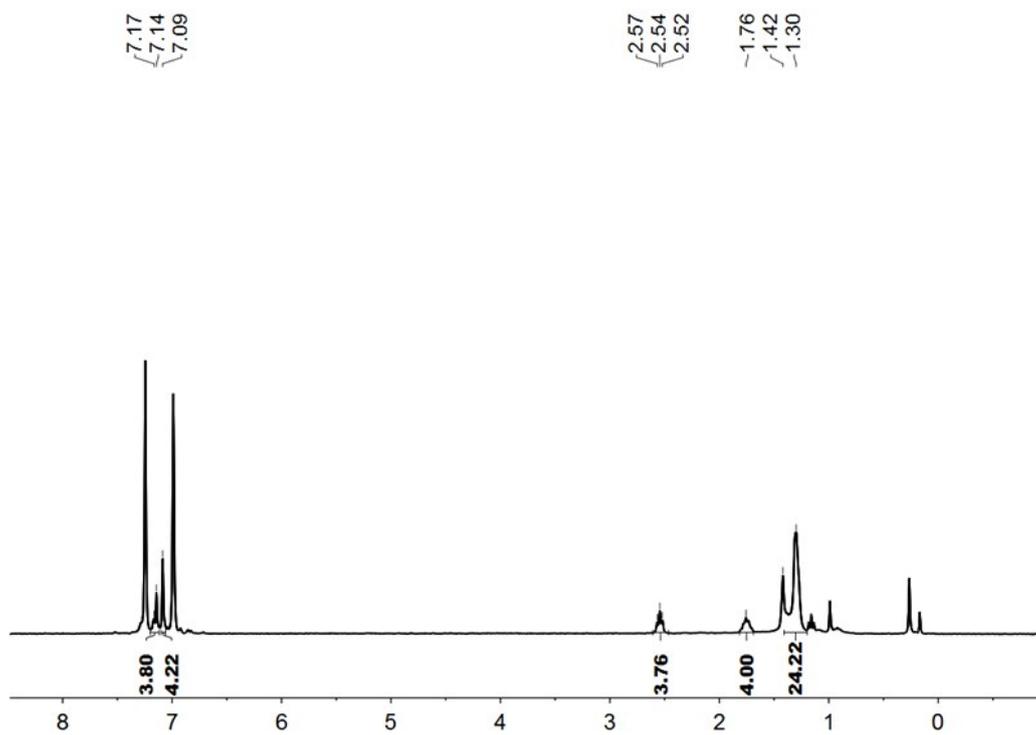


Figure S15. ^1H NMR spectrum of P2.

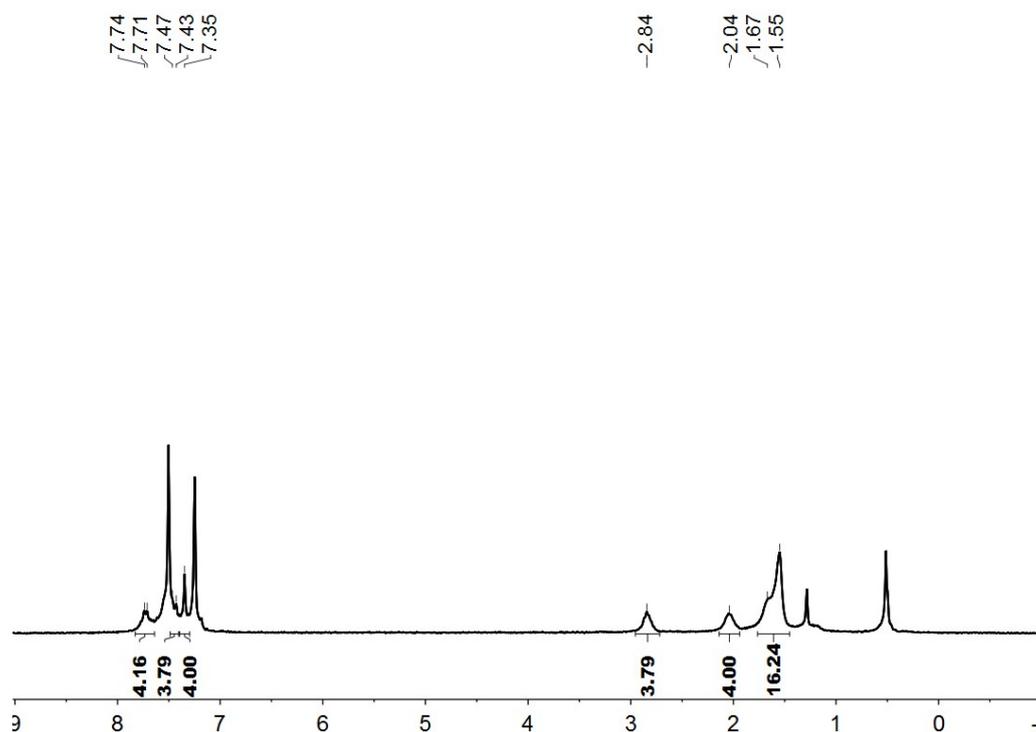


Figure S16. ^1H NMR spectrum of P3.

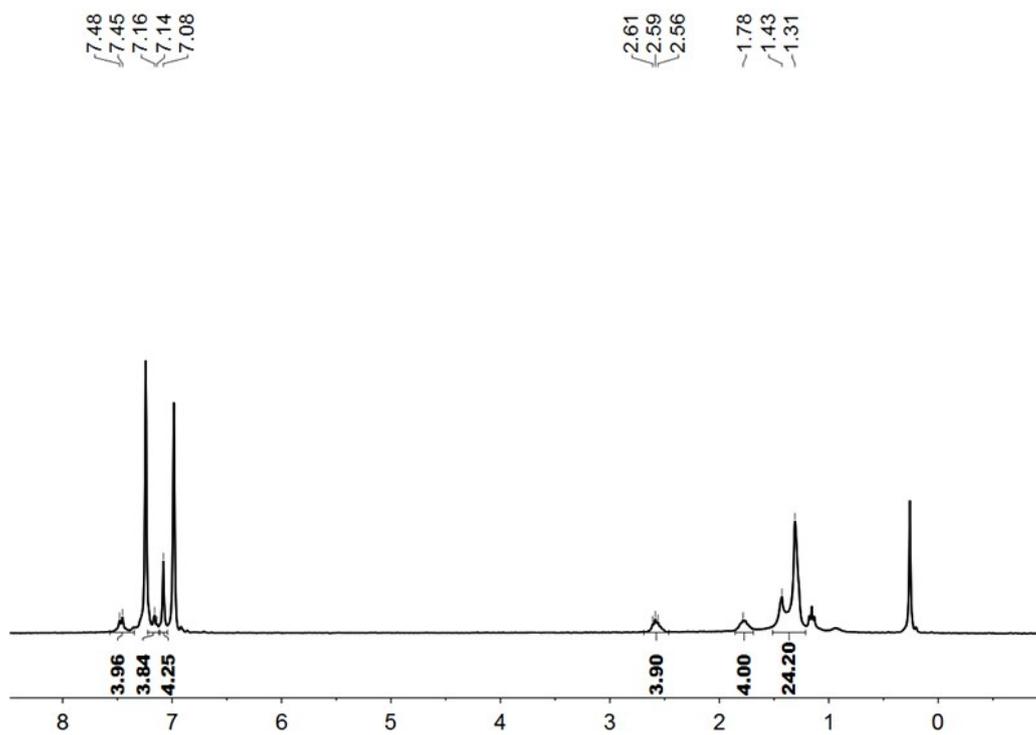


Figure S17. ^1H NMR spectrum of P4.

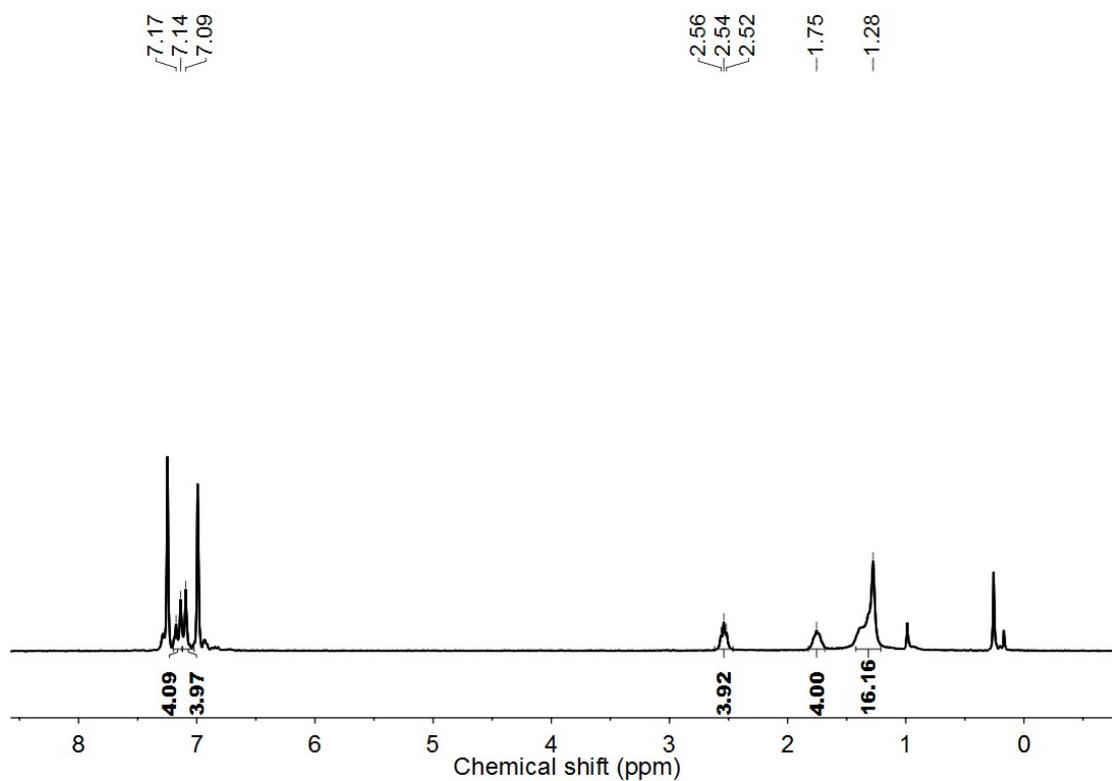


Figure S18. ^1H NMR spectrum of the precipitate.

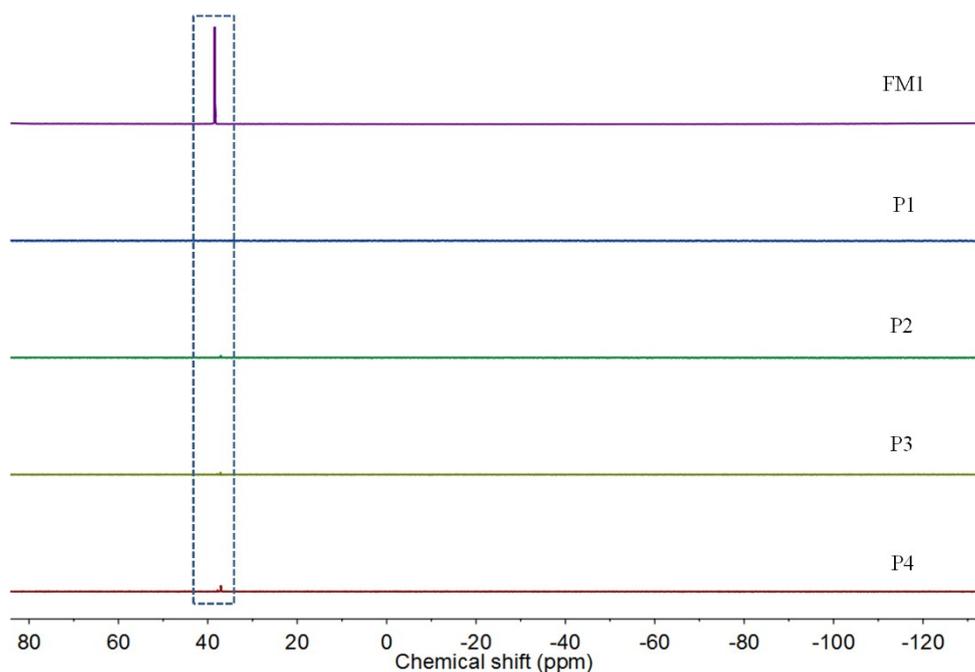


Figure S19. ^{19}F NMR spectra of **FM1**, **P1**, **P2**, **P3** and **P4**.

Table S1. Mesomorphic Properties of the Monomers and Polymers^a

Monomers	Phase transitions (°C)	Polymers	Phase transitions (°C)
SiM1	K 47 I I 18 K	P1	G 135 X 141 N 169 I I 122 N 106 G
SiM2	K 69 I I 46 K	P2	G 123 N 160 I I 108 G
SiM3	K 120 I I 105 K	P3	G 131 N 182 I I 171 N 120 G
SiM4	K 69 N 103 I I 74 N 64 K	P4	G 99 N 162 I I 159 N 87 G
FM1	K 78 I I 59 K		

^aDetermined by the combination of POM and DSC. K = crystalline, G = glass phase, N = nematic phase, I = isotropic phase, X = unidentified phase. First line obtained on heating, second line obtained on cooling.

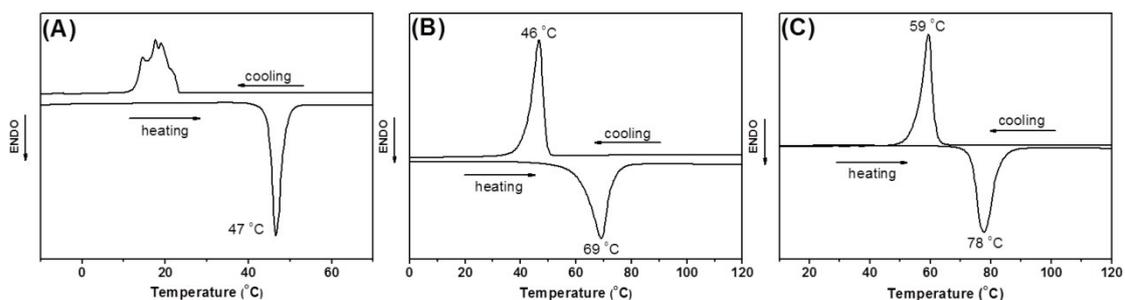


Figure S20. DSC curves of (A) SiM1, (B) SiM2, and (C) FM1.



Figure S21. POM images of (A) SiM1, (B) SiM2, (C) FM1.

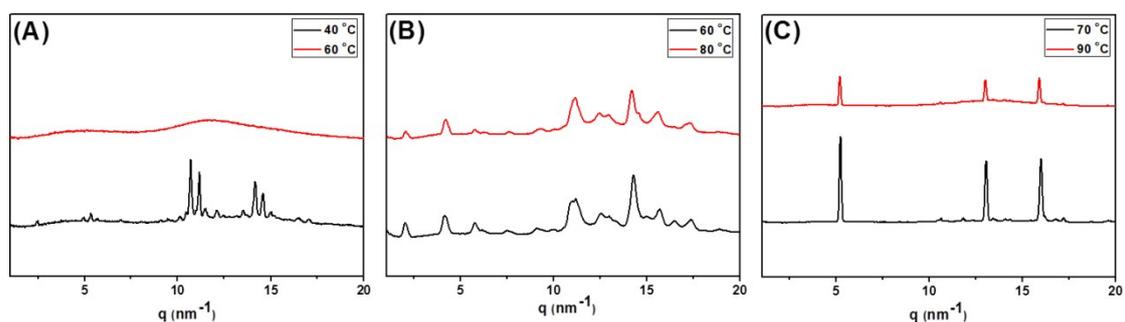


Figure S22. 1D-WAXS patterns of (A) SiM1, (B) SiM2, (C) FM1.

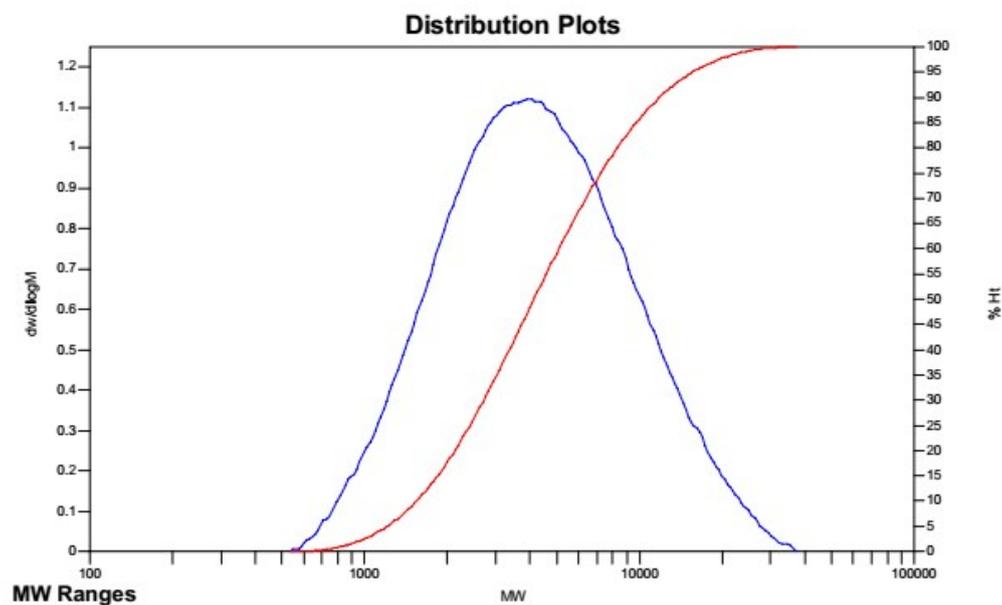
Table S2. SuFEx reaction conditions and the corresponding polymerization results.

Entry	Polymer	Solvent	Catalysts	Temp./°C	Mn (g/mol)	Mw(g/mol)	PDI
1	P1	NMP	DBU	r.t.	3140	5600	1.79
2	P1	DMF	DBU	r.t.	3180	4260	1.34
3	P1	TCB	DBU	r.t.	5360	8540	1.59
4	P1	TCB	DBU	80	6910	15280	2.21
5	P1	TCB	DBU	120	3850	6000	1.56
6	P1	TCB	TBD	80	2540	4660	1.84
7	P1	TCB	BEMP	80	1930	2990	1.55

Entry1 of Table S2

MW Averages

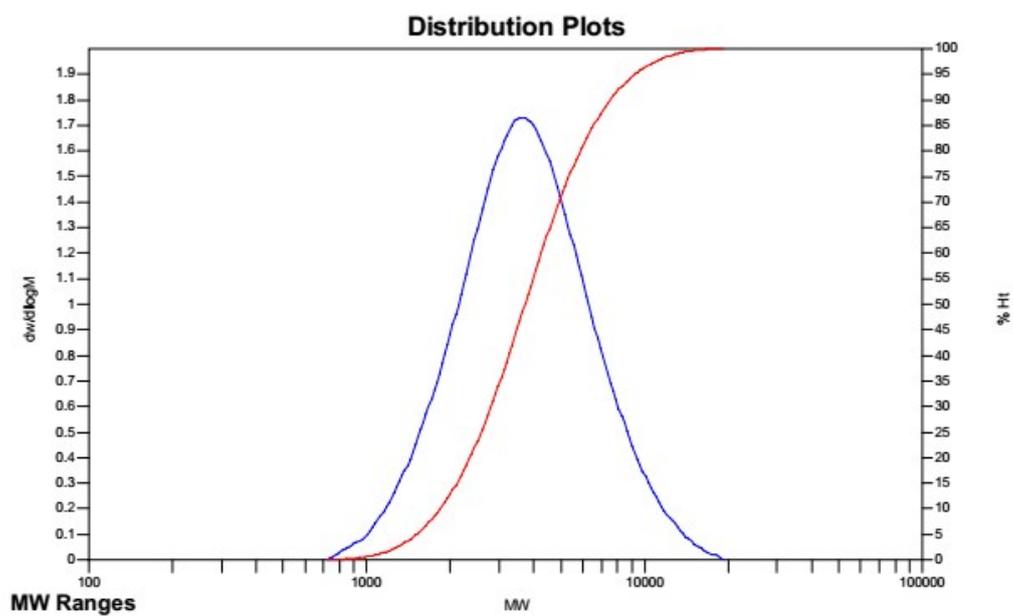
Mp: 3890 Mn: 3136 Mv: 5128 Mw: 5599
Mz: 9617 Mz+1: 14318 PD: 1.7854



Entry 2 of Table S2

MW Averages

Mp: 3641 Mn: 3182 Mv: 4076 Mw: 4258
Mz: 5661 Mz+1: 7324 PD: 1.3382

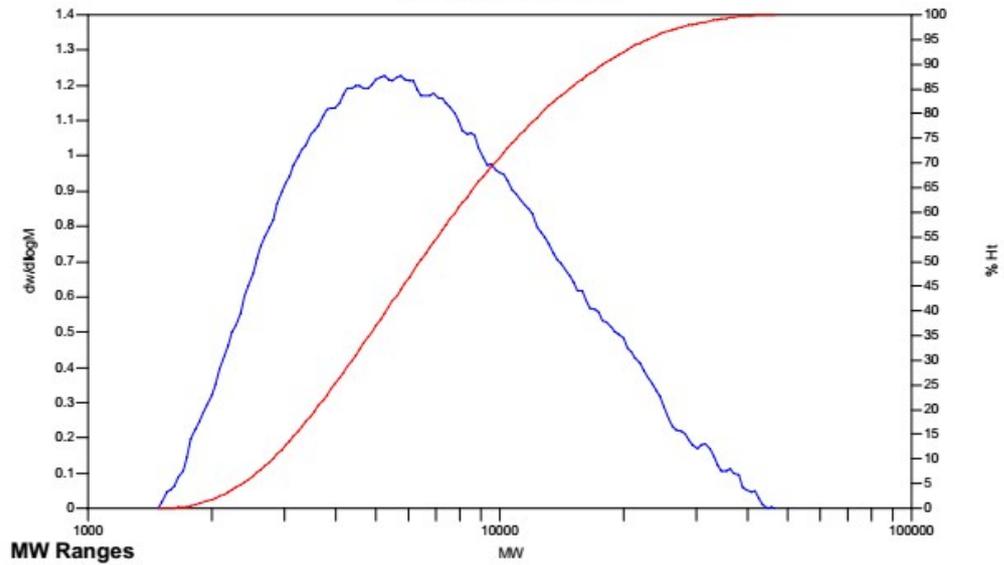


Entry 3 of Table S2

MW Averages

Mp: 5752 Mn: 5358 Mv: 7919 Mw: 8535
Mz: 13690 Mz+1: 19519 PD: 1.5929

Distribution Plots

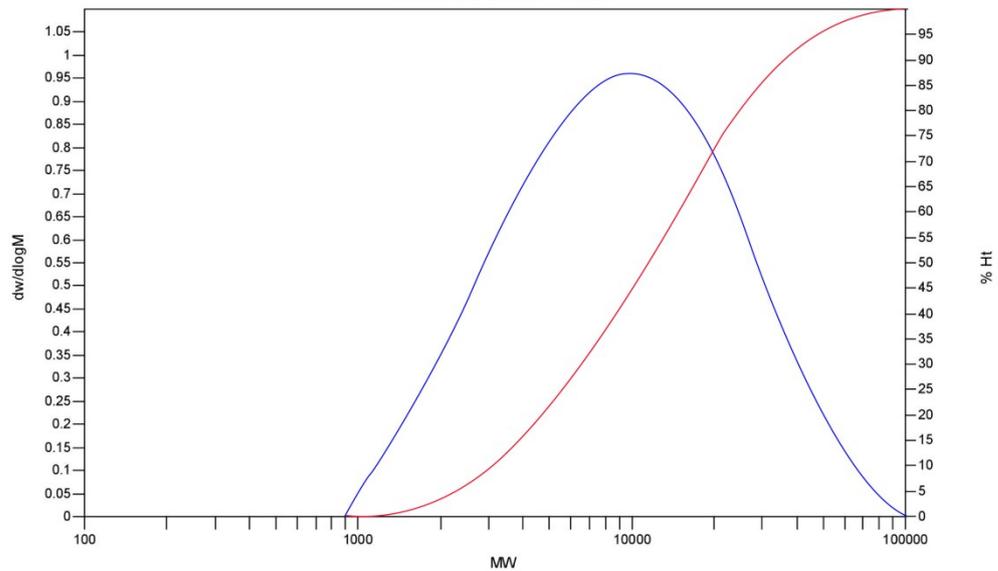


Entry 4 of Table S2

MW Averages

Mp: 9988 Mn: 6908 Mv: 13765 Mw: 15275
Mz: 27372 Mz+1: 39456 PD: 2.2112

Distribution Plots



Entry 5 of Table S2

MW Averages

Mp: 3801

Mn: 3847

Mv: 5588

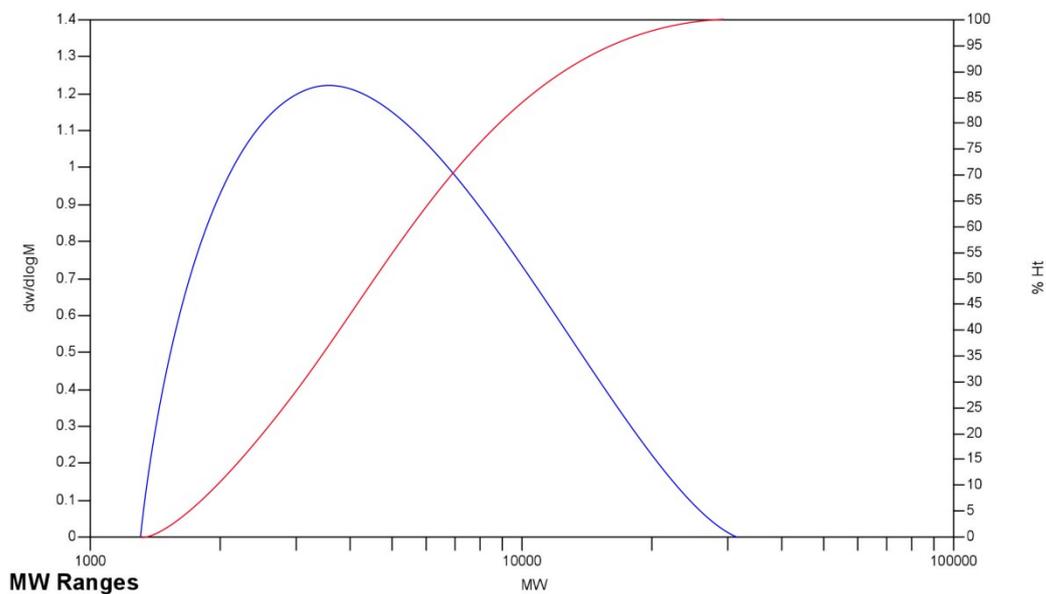
Mw: 5999

Mz: 9343

Mz+1: 12985

PD: 1.5594

Distribution Plots



Entry 6 of Table S2

MW Averages

Mp: 3630

Mn: 2535

Mv: 4277

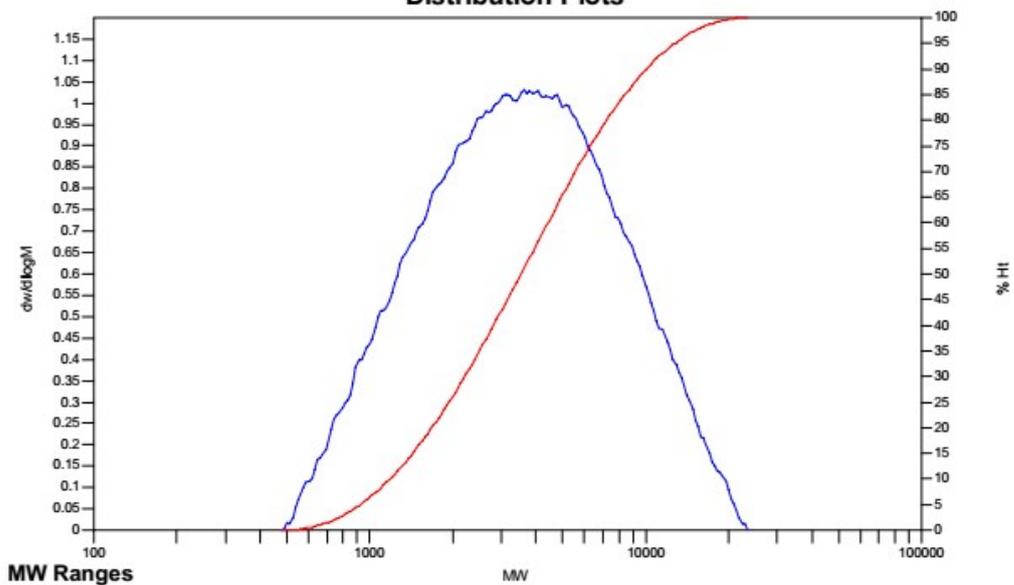
Mw: 4663

Mz: 7676

Mz+1: 10601

PD: 1.8394

Distribution Plots



Entry 7 of Table S2

MW Averages

Mp: 2291

Mn: 1933

Mv: 2801

Mw: 2989

Mz: 4491

Mz+1: 6180

PD: 1.5463

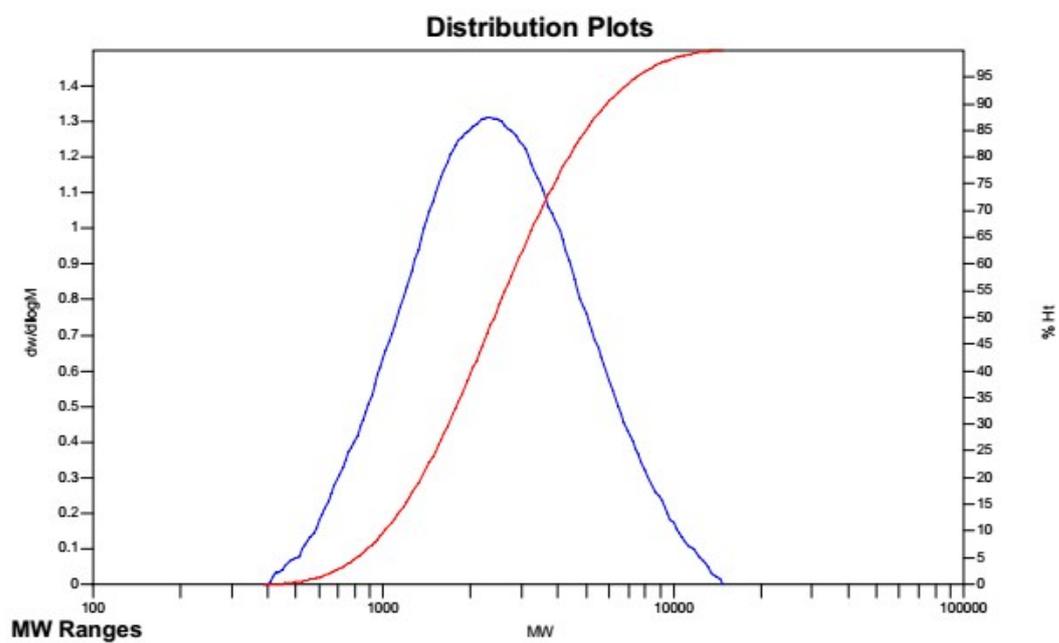


Table S3. Polymerization of fluoro-terminal monomer **FM1** and silyl-terminal monomer **SiM1-4** performed at 80 °C in TCB for 12 h by using DBU (20 mol%) as catalyst.

Entry	Monomer	Monomer	Polymer	Mn(g/mol)	Mw(g/mol)	PDI	Yield (%)
1	FM1	SiM1	P1	6910	15280	2.21	57
2	FM1	SiM2	P3	10020	13800	1.46	61
3	FM1	SiM3	P2	6610	12900	1.95	48
4	FM1	SiM4	P4	6680	13130	1.97	45

Entry 1 of Table S3

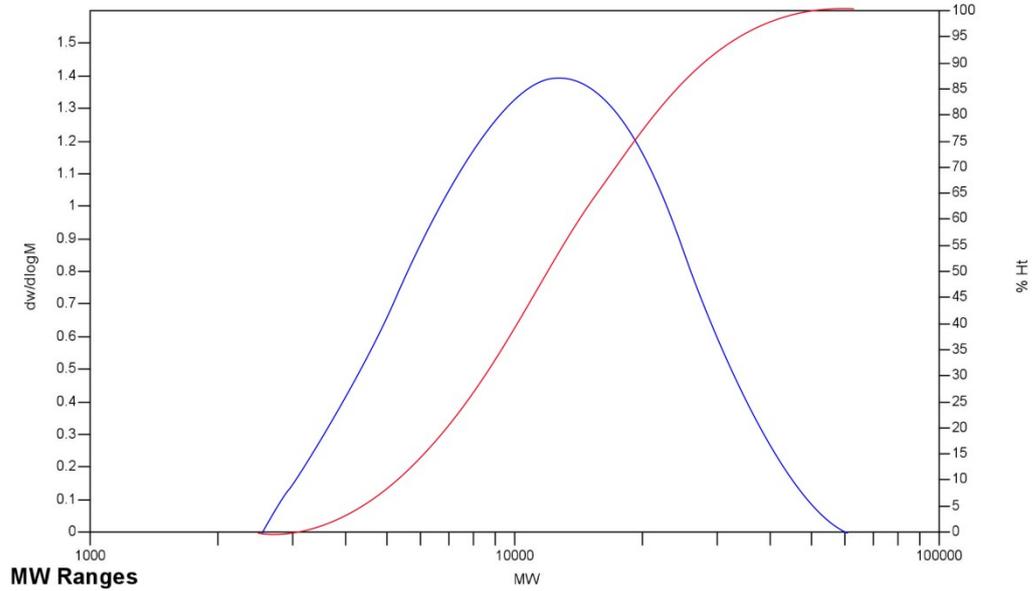


Entry 2 of Table S3

MW Averages

Mp: 12873 Mn: 10018 Mv: 13802 Mw: 14590
Mz: 20572 Mz+1: 26876 PD: 1.4564

Distribution Plots

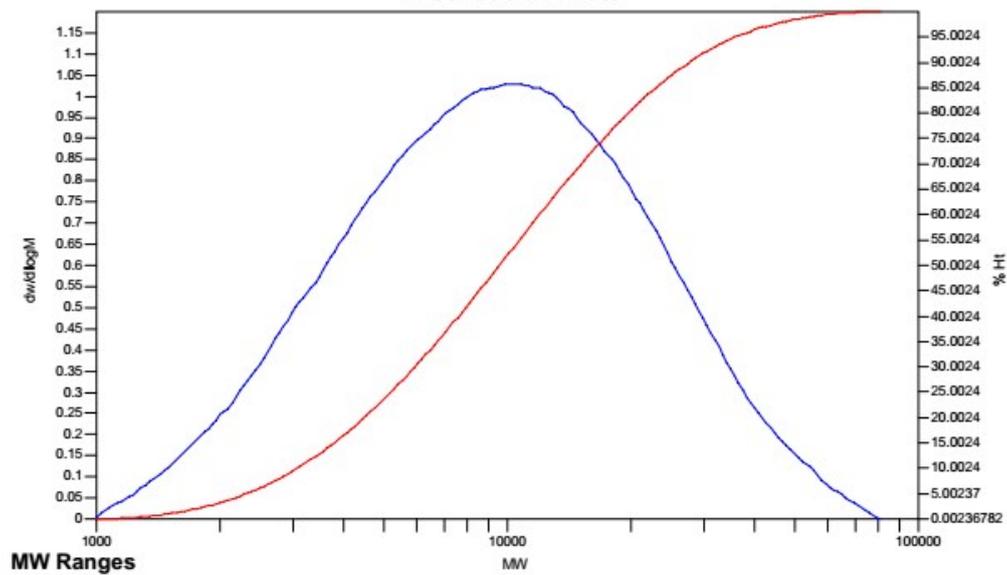


Entry 3 of Table S3

MW Averages

Mp: 10325 Mn: 6610 Mv: 11726 Mw: 12877
Mz: 22295 Mz+1: 32416 PD: 1.9481

Distribution Plots



Entry 4 of Table S3

MW Averages

Mp: 12029

Mn: 6678

Mv: 11989

Mw: 13127

Mz: 22059

Mz+1: 31052

PD: 1.9657

